



**Continuous solid solutions of Na<sub>0.5</sub>La<sub>0.5</sub>TiO<sub>3</sub>–LaCrO<sub>3</sub> for photocatalytic H<sub>2</sub> evolution under visible-light irradiation**

|                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|-------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Journal:                      | <i>RSC Advances</i>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
| Manuscript ID                 | RA-ART-03-2016-007891.R1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| Article Type:                 | Paper                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |
| Date Submitted by the Author: | 19-May-2016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| Complete List of Authors:     | <p>Shi, Jinwen; Xi'an Jiaotong University (XJTU), State Key Laboratory of Multiphase Flow in Power Engineering (MFPE); Xi'an Jiaotong University (XJTU), Department of New Energy Science and Engineering, School of Energy and Power Engineering</p> <p>Zong, Shichao; Xi'an Jiaotong University (XJTU), State Key Laboratory of Multiphase Flow in Power Engineering (MFPE)</p> <p>Hu, Yuchao; Xi'an Jiaotong University (XJTU), State Key Laboratory of Multiphase Flow in Power Engineering (MFPE)</p> <p>Guan, Xiangjiu; Xi'an Jiaotong University (XJTU), State Key Laboratory of Multiphase Flow in Power Engineering (MFPE)</p> <p>Luo, Jiaying; Xi'an Jiaotong University (XJTU), Department of New Energy Science and Engineering, School of Energy and Power Engineering</p> <p>Shang, Yi; Xi'an Jiaotong University (XJTU), Department of New Energy Science and Engineering, School of Energy and Power Engineering</p> <p>Li, Guoxing; Xi'an Jiaotong University (XJTU), Department of New Energy Science and Engineering, School of Energy and Power Engineering</p> <p>Liu, Dongyu; Xi'an Jiaotong University (XJTU), Department of New Energy Science and Engineering, School of Energy and Power Engineering</p> <p>Wang, Xing; Xi'an Jiaotong University (XJTU), Department of New Energy Science and Engineering, School of Energy and Power Engineering</p> <p>Guo, Penghui; Xi'an Jiaotong University, State Key Laboratory of Multiphase Flow in Power Engineering (MFPE); Xi'an Jiaotong University (XJTU), Department of New Energy Science and Engineering, School of Energy and Power Engineering</p> |
| Subject area & keyword:       | Photocatalysis < Catalysis                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
|                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |



Journal Name

ARTICLE

## Continuous solid solutions of $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3\text{--LaCrO}_3$ for photocatalytic $\text{H}_2$ evolution under visible-light irradiation†

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Jinwen Shi,<sup>a,b,\*</sup> Shichao Zong,<sup>a</sup> Yuchao Hu,<sup>a</sup> Xiangjiu Guan,<sup>a</sup> Jiaying Luo,<sup>b</sup> Yi Shang,<sup>b</sup> Guoxing Li,<sup>b</sup> Dongyu Liu,<sup>b</sup> Xin Wang<sup>b</sup> and Penghui Guo<sup>a,b,\*</sup>

A series of continuous  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with orthorhombic-phase perovskite structure and with  $\text{LaCrO}_3$  contents ( $x$ ) in the range from 0 to 1.0 were synthesized by a facile polymerized complex method, and were employed as photocatalysts for  $\text{H}_2$  evolution under visible-light irradiation. It was found that photocatalytic activities of the solid solutions significantly increased with the increase of  $x$  to 0.3, and reached the highest  $\text{H}_2$ -evolution rate of  $238.2 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$  on  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{0.7}(\text{LaCrO}_3)_{0.3}$ , because the narrowed bandgaps of samples enhanced the generation of charge carriers and the increased lattice distortion of samples could promote the separation and migration of charge carriers. Nevertheless, photocatalytic activities of the solid solutions gradually decreased with the further increase of  $x$  from 0.3, since both the bandgaps and lattice distortion rarely changed but  $\text{Cr}^{6+}$  and defects gradually increased and thus accelerated the recombination of charge carriers.

### Introduction

Photocatalytic  $\text{H}_2$  production from  $\text{H}_2\text{O}$  under solar-light irradiation has drawn more and more attention, because the deepening global problems of energy crisis and environmental pollution could be expected to be solved simultaneously based on such a solar-to-hydrogen conversion process.<sup>1–5</sup> The exploitation of visible-light-driven photocatalysts with low-cost, high stability and high efficiency has been accepted as one of the key issues in this research field since the energy of visible light accounts for around 43% of the incoming solar energy,<sup>6</sup> and many milestone achievements have been acquired during the past few decades.<sup>6–11</sup>

$\text{ABO}_3$  perovskite materials have been considered as promising candidates functioning as such photocatalysts,<sup>1,12,13</sup> because the adjustable crystal structures and chemical compositions provided extensive space to modify the existing materials and develop new materials that were well competent for visible-light-drive photocatalytic  $\text{H}_2$  production.<sup>1</sup> It was reported in our previous work that  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1.00}(\text{LaCrO}_3)_y$  solid solutions with cubic-phase perovskite structure were prepared by a hydrothermal method

for the first time and showed stable photocatalytic  $\text{H}_2$ -evolution activity under visible-light irradiation,<sup>14</sup> although both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  were not active for such a photocatalytic reaction due to the wide bandgap of  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  incapable of utilizing visible light and the low conduction band (CB) level of  $\text{LaCrO}_3$  unsuitable for reducing  $\text{H}_2\text{O}$  to  $\text{H}_2$ . Nevertheless,  $\text{LaCrO}_3$  contents in  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1.00}(\text{LaCrO}_3)_y$  solid solutions were severely limited and  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1.00}(\text{LaCrO}_3)_y$  solid solutions with  $y$  only no more than 0.2 could be obtained due to the employed hydrothermal process, during which Cr with higher concentration held back the growth of crystals and could not incorporate into the crystal lattices of cubic-phase perovskite and finally leaked out. The limited  $\text{LaCrO}_3$  contents in  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1.00}(\text{LaCrO}_3)_y$  solid solutions restricted the adjustment and optimization of physiochemical properties, especially the electronic band structures, and hence were unfavorable for the further enhancement of photocatalytic performance.

Herein, a series of continuous  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with  $\text{LaCrO}_3$  contents ( $x$ ) in the range from 0 to 1.0 were synthesized by a facile polymerized complex (PC) method instead of the hydrothermal method employed in our previous work, in order to optimize the physiochemical properties by adjusting the chemical compositions over a larger range and thus attempt to further improve the photocatalytic performance.

### Experimental

#### Materials and sample preparation

<sup>a</sup> International Research Center for Renewable Energy (IRCRe), State Key Laboratory of Multiphase Flow in Power Engineering (MFPE), Xi'an Jiaotong University (XJTU), 28 West Xianning Road, Xi'an 710049, China. Email: jinwen\_shi@mail.xjtu.edu.cn (J.W. Shi), ph-guo@mail.xjtu.edu.cn (P.H. Guo).

<sup>b</sup> Department of New Energy Science and Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University (XJTU), 28 West Xianning Road, Xi'an 710049, China. Email: jinwen\_shi@mail.xjtu.edu.cn (J.W. Shi), ph-guo@mail.xjtu.edu.cn (P.H. Guo).

† Electronic Supplementary Information (ESI) available: Calculation of quantum efficiency; Raman spectrum of as-prepared  $\text{LaCrO}_3$ ; SEM images of  $\text{NaLaTiCrO}_3\text{--}x$  samples; BET surface areas of  $\text{NaLaTiCrO}_3\text{--}x$  samples. See DOI: 10.1039/x0xx00000x

Methanol, citric acid monohydrate, tetrabutyl titanate, sodium nitrate, chromium nitrate nonahydrate, ethylene glycol were of analytical reagent (AR) grade and used as received from Sinopharm Chemical Reagent Co., Ltd. Lanthanum nitrate hexahydrate was of rare earth oxide (REO) grade and used as received from Alfa Aesar.

$(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  ( $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$  and  $1.0$ ) solid solutions were prepared by a facile PC method,<sup>15-17</sup> and the typical procedure was described as follows. Citric acid monohydrate (0.04 mol) was dissolved in methanol (50 mL) to form a clear solution, into which Ti source (tetrabutyl titanate), La source (lanthanum nitrate hexahydrate), Na source (sodium nitrate) and Cr source (chromium nitrate nonahydrate), with the amounts calculated according to the stoichiometric ratio of  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  (0.01 mol), was dissolved in sequence, and then ethylene glycol (0.16 mol) was added. The resulting transparent solution was heated by oil bath in a fume hood at 75 °C for 4 h and 130 °C for 24 h in sequence to remove excess solvent and promote polymerization. The whole process above was accompanied with magnetic stirring. The obtained glassy resin was then sequentially pyrolyzed in a burnout furnace at 200, 300 and 500 °C for 6 h, 3 h and 6 h, respectively. The resulting powder was calcined in a muffle furnace under ambient atmosphere at 1100 °C for 6 h to facilitate the crystallization and to get the final product with name abbreviated as NaLaTiCrO- $x$  ( $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$  and  $1.0$ ).

#### Characterization of samples

X-ray diffraction (XRD) patterns were measured by a PANalytical X'pert Pro MPD diffractometer using Ni-filtered Cu K $\alpha$  irradiation ( $\lambda = 1.5406 \text{ \AA}$ , 40 kV, 40 mA) and a scan rate of  $1^\circ \text{ min}^{-1}$  in the  $2\theta$  range from  $10^\circ$  to  $80^\circ$ . Fourier transform infrared spectra (FTIR) were recorded between 1000 and  $400 \text{ cm}^{-1}$  on a Bruker Vertex 70 spectrophotometer. Raman spectra were measured by a Horiba/Jobin Yvon LabRAM HR 800 Fourier-transform laser micro-Raman spectrometer with a backscattering configuration and an Ar<sup>+</sup> laser (514.532 nm) as the excitation source. UV-Vis absorption spectra were recorded with a Hitachi U-4100 spectrophotometer under

diffuse-reflectance mode using BaSO<sub>4</sub> as reference. X-ray photoelectron spectroscopy (XPS) data were collected from a Kratos Axis Ultra DLD instrument with a monochromatized Al K $\alpha$  line source (150 W), and all binding energies were referenced to the adventitious C 1s peak at 284.8 eV. Field-emission scanning electron microscopy (FESEM) images were observed by a JEOL JSM-7800F instrument. BET surface areas were obtained by N<sub>2</sub> adsorption using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer after the degasification of samples at 250 °C for 3 h.

#### Photocatalytic test of samples

Photocatalytic test of samples for H<sub>2</sub> evolution under visible-light irradiation was performed in a Pyrex glass cell with a side window for external-light incidence. A 300W Xe arc lamp with a UV-cutoff filter ( $\lambda > 420 \text{ nm}$ ) was used as light source. Sample (0.100 g) was dispersed into HCOOH solution (10 vol%, 200 mL), in which HCOOH acted as sacrificial reagent. Pt (0.5 wt%) cocatalyst was photodeposited in situ on samples by using an appropriate amount of H<sub>2</sub>PtCl<sub>6</sub> aqueous solution as Pt precursor. After purged with N<sub>2</sub> to eliminate air, the dispersion was irradiated, with a constant stirring velocity and at a constant temperature around 35 °C. The evolved H<sub>2</sub> was analyzed by a gas chromatograph with a TDX-01 column, a thermal conductivity detector, and Ar as carrier gas.

## Results and discussion

Fig. 1a shows XRD patterns of NaLaTiCrO- $x$  samples. All samples showed analogous XRD patterns, in which all diffraction peaks were well matched with Na<sub>0.5</sub>La<sub>0.5</sub>TiO<sub>3</sub> (JCPDS no. 01-089-6954) and LaCrO<sub>3</sub> (JCPDS no. 01-089-8770) with similar orthorhombic-phase perovskite structure (space group, *pnma*). It was thus demonstrated that a series of high-purity, single-phase materials with continuously adjusted compositions, i.e., continuous solid solutions of  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  with  $x$  in the range from 0 to 1.0, were successfully prepared. It was reported in our previous work that  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1.00}(\text{LaCrO}_3)_y$  solid solutions with  $y$  no more than 0.2 were prepared by hydrothermal method and

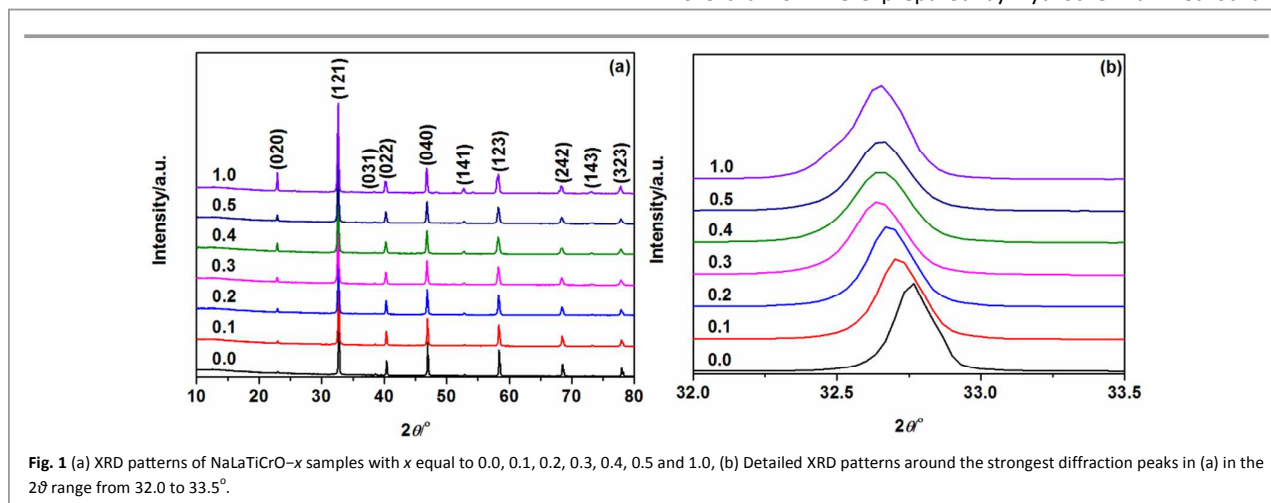
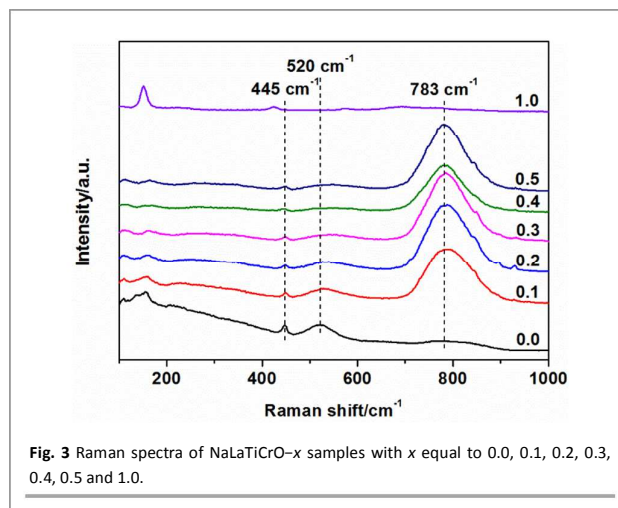
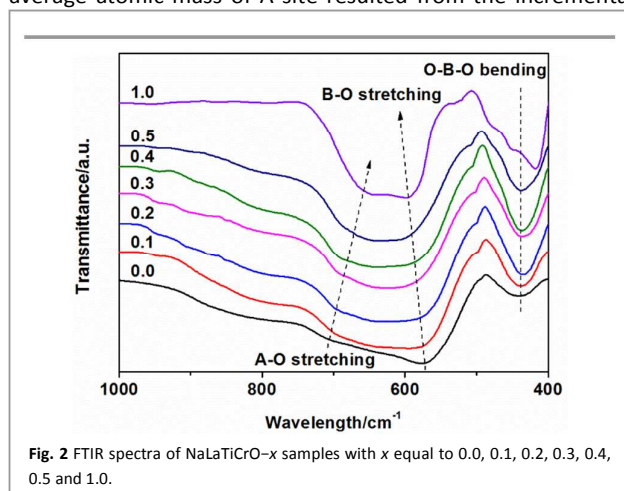


Fig. 1 (a) XRD patterns of NaLaTiCrO- $x$  samples with  $x$  equal to 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0, (b) Detailed XRD patterns around the strongest diffraction peaks in (a) in the  $2\theta$  range from  $32.0$  to  $33.5^\circ$ .

showed cubic-phase perovskite structure.<sup>14</sup> However,  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1.00}(\text{LaCrO}_3)_y$  with higher  $\text{LaCrO}_3$  contents could not be obtained by such a hydrothermal process, since Cr with higher concentration held back the growth of crystals and could not incorporate into the crystal lattices of cubic-phase perovskite and finally leaked out. In contrast, on the one hand, the PC method employed in this work guaranteed the successful preparation of continuous solid solutions of  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  with  $\text{LaCrO}_3$  contents in the range from 0 to 1.0, since such a process avoided the segregation of phases and the leakage of metal elements;<sup>15-17</sup> on the other hand, the PC method resulted in perovskite structure with orthorhombic phase instead of cubic phase maybe due to the process at temperature (1100 °C) higher than that (180 °C) during the hydrothermal process. Furthermore, Fig. 1b shows the detailed XRD patterns around the strongest diffraction peaks corresponding to (121) planes of orthorhombic-phase perovskite  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$ . It was found that the (121) diffraction peak gradually shifted toward a lower angle with the increasing of  $x$ . Such peak shift was often observed in solid-solution materials with the change of compositions and was generally recognized as the evidence for the successful formation of solid solutions.<sup>18,19</sup> Since  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  has a tolerance factor (0.979) larger than that of  $\text{LaCrO}_3$  (0.969), the increased incorporation of  $\text{LaCrO}_3$  member into  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  member would cause further distortion of  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  members, and hence led to the peak shift.<sup>14</sup>

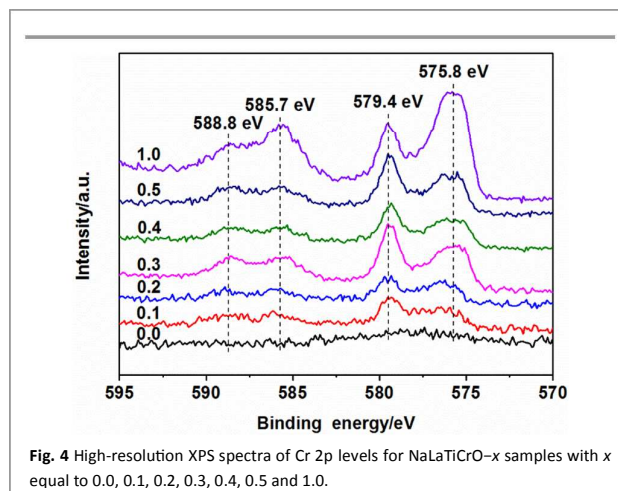
Fig. 2 displays the FTIR spectra of  $\text{NaLaTiCrO-x}$  samples. Three strong characteristic absorption bands were located at around 440, 575 and 650  $\text{cm}^{-1}$ , which were ascribed to the bending vibration of O-B-O bonding, the stretching vibration of B-O bonding, and the stretching vibration of A-O bonding, respectively.<sup>20,21</sup> Furthermore, with the increase of  $x$ , the band corresponding to B-O stretching vibration gradually blueshifted due to the further distortion of  $\text{BO}_6$  octahedra caused by the incremental incorporation of  $\text{LaCrO}_3$  member as proved by XRD results,<sup>20</sup> and the band corresponding to A-O stretching vibration gradually redshifted because of the increased average atomic mass of A site resulted from the incremental



incorporation of La element that is heavier than Na element.

Fig. 3 exhibits Raman spectra of  $\text{NaLaTiCrO-x}$  samples. Three characteristic bands appeared at around 445, 520 and 783  $\text{cm}^{-1}$  in all  $\text{NaLaTiCrO-x}$  samples except  $\text{LaCrO}_3$ . It is generally considered that the high-frequency bands are associated with the vibrations of  $\text{BO}_6$  octahedra.<sup>22,23</sup> Compared with  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$ ,  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  members showed significantly enhanced peaks at 783  $\text{cm}^{-1}$ , which confirmed the further distortion of  $\text{BO}_6$  octahedra caused by the incorporation of  $\text{LaCrO}_3$  member into  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  member as evidenced by XRD and FTIR results.<sup>22,23</sup> Besides, The as-prepared  $\text{LaCrO}_3$  presented Raman spectrum (Fig. 3 and S1) in agreement with the reported results,<sup>24,25</sup> but distinctly different from those of other  $\text{NaLaTiCrO-x}$  samples, which reflected the different local microstructure in  $\text{LaCrO}_3$ .<sup>26</sup>

In order to analyze the contents and chemical states of Cr in  $\text{NaLaTiCrO-x}$  samples, high-resolution XPS spectra of Cr 2p levels were recorded and are shown in Fig. 4. All Cr-containing samples comprised two pairs of spin-orbit doublets, thus indicating that Cr species had two types of chemical states. The pair of Cr 2p split orbits with binding energies of 575.8 eV



(Cr  $2p_{3/2}$ ) and 585.7 eV (Cr  $2p_{1/2}$ ) was assigned to Cr<sup>3+</sup>, and the other pair of Cr 2p split orbits with binding energies of 579.4 eV (Cr  $2p_{3/2}$ ) and 588.8 eV (Cr  $2p_{1/2}$ ) was allocated to Cr<sup>6+</sup>.<sup>27-29</sup> It was reported in our previous work that only Cr<sup>3+</sup> existed in the hydrothermally prepared  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1.00}(\text{LaCrO}_3)_y$  solid solutions, because the low-temperature process prevented further oxidation of Cr<sup>3+</sup>.<sup>14</sup> In contrast, the PC method resulted in the existence of Cr<sup>6+</sup> besides Cr<sup>3+</sup> due to the high-temperature process. It is reasonable to deduce that Cr<sup>6+</sup> content in NaLaTiCrO-*x* samples would raise up with the increase of *x* due to the raise of total Cr content.

Fig. 5 displays UV-Vis spectra of NaLaTiCrO-*x* samples.  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  showed an absorption edge at around 390 nm corresponding to a bandgap of 3.19 eV, thus implying that the absorption from band-to-band transition was limited in the UV light region. Besides, a weak absorption tail appeared in the region with wavelength longer than 390 nm, and was ascribed to the surface states and defect levels caused by the high-temperature process.<sup>30,31</sup> In contrast, such an absorption tail was not detected on the hydrothermally prepared  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  due to trait of perfect single crystal with few lattice defects as reported in our previous work.<sup>14</sup> All  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  members samples exhibited intense band-to-band absorption in the region with wavelength longer than 390 nm, and was ascribed to the surface states and defect levels caused by the high-temperature process.<sup>30,31</sup> In contrast, such an absorption tail was not detected on the hydrothermally prepared  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  due to trait of perfect single crystal with few lattice defects as reported in our previous work.<sup>14</sup> All  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  members samples exhibited intense band-to-band absorption in the visible-light region, thus confirming the effective extension of light response by the incorporation of  $\text{LaCrO}_3$  member into  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  member to form new energy bands. Furthermore, with the increase of *x* in NaLaTiCrO-*x* samples, the light-absorption edges were gradually redshifted (to around 550 nm) and the absorption coefficients were improved (with the absorbance to 1.0). The results were consistent with the variation of sample colors from grayish white to yellow that became deeper with the increase of *x*, and demonstrated the enhancement of visible-light-response ability, and reflected the gradual change of electronic band structures in  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions. According to the results of theoretical calculations on electronic band structures using the first-principles method,<sup>14</sup> the CB and valence band (VB) of  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  was mainly made up of Ti 3d orbitals and O 2p orbitals, respectively, and the CB and VB of  $\text{LaCrO}_3$  mainly consisted of Cr 3d  $e_g$  orbitals and Cr 3d  $t_{2g}$  orbitals, respectively. As for  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  members, the CB was composed of the hybrid orbitals of Cr 3d  $e_g$  and Ti 3d and the VB was made up of Cr 3d  $t_{2g}$  orbitals. It is reasonable to deduce that, with the increase of *x*, the CB of  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  members could

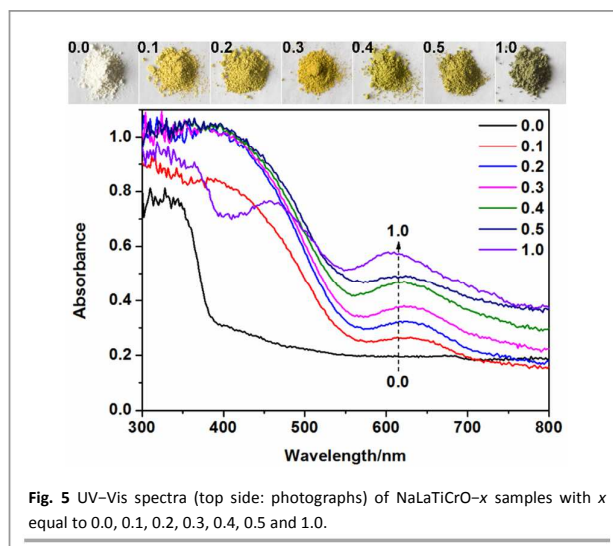


Fig. 5 UV-Vis spectra (top side: photographs) of NaLaTiCrO-*x* samples with *x* equal to 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0.

be adjusted and should be located between those of  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  by the hybridization of Ti 3d orbitals and Cr 3d  $e_g$  with varied ratios, thereby affecting the bandgap as evidenced by the gradual shift of light-absorption edge in the UV-Vis spectra. Besides, with the increase of *x*, an absorption hump appeared around 620 nm and gradually enhanced due to d-d transition of Cr<sup>3+</sup> in  $\text{BO}_6$  octahedra.<sup>27</sup> In addition, with the increase of *x* in Cr-containing samples, an absorption tail appeared in the region with wavelength longer than 700 nm and gradually enhanced due to the incremental surface states and defect levels (e.g., oxygen vacancy states,<sup>27</sup>),<sup>30,31</sup> which was in consistency with the change of sample color that became less bright.<sup>31</sup>

Fig. 6a presents the photocatalytic H<sub>2</sub>-evolution activity of NaLaTiCrO-*x* samples under visible-light irradiation. No H<sub>2</sub> was detected in the absence of either NaLaTiCrO-*x* samples or light irradiation whereas keeping other conditions the same, thereby announcing that neither photolysis of HCOOH nor non-photocatalytic effect (e.g., mechanocatalysis) of NaLaTiCrO-*x* samples contributed to H<sub>2</sub> evolution. Owing to the wide bandgap unsuitable for utilizing visible light,  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  showed only a trace amount of H<sub>2</sub> evolution that was induced by the surface states and defect levels as proved by UV-Vis results. Due to the low CB level that results in weak driving force for reducing H<sub>2</sub>O to H<sub>2</sub>,  $\text{LaCrO}_3$  showed negligible H<sub>2</sub> evolution although this material has a bandgap narrow enough to absorb visible light. However, it was noteworthy that all  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  members exhibited noticeable H<sub>2</sub> evolution. It was thus demonstrated that construction of solid solution based on  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  materials is an effective strategy to develop visible-light-driven H<sub>2</sub>-evolution photocatalysts, which have electronic band structures suitable for both visible-light absorption and H<sub>2</sub>O reduction. Furthermore, photocatalytic activities of  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  members significantly increased with the increase of *x*, and reached the highest H<sub>2</sub>-evolution rate of 238.2  $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$

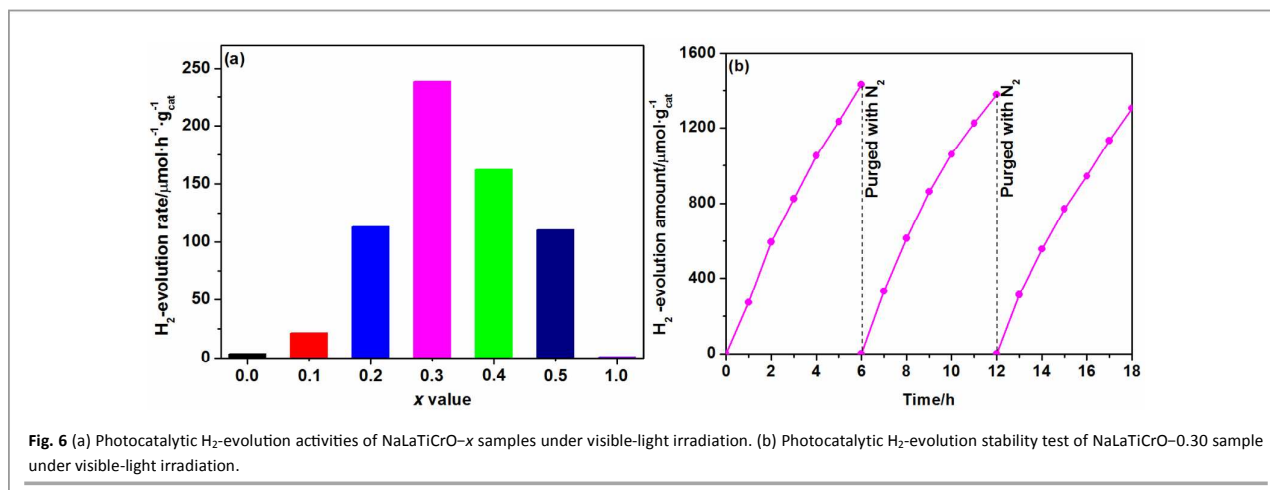


Fig. 6 (a) Photocatalytic H<sub>2</sub>-evolution activities of NaLaTiCrO-x samples under visible-light irradiation. (b) Photocatalytic H<sub>2</sub>-evolution stability test of NaLaTiCrO-0.30 sample under visible-light irradiation.

on NaLaTiCrO-0.3, but gradually decreased with the further increase of  $x$ . The apparent quantum efficiency on NaLaTiCrO-0.30 was estimated to be 0.57% at  $425 \pm 10$  nm (see the calculation of quantum efficiency in the Electronic Supplementary Information). It should be noted that all  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with both  $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$  and  $\text{LaCrO}_3$  members showed similar surface morphologies (Fig. S2) and comparable Brunauer-Emmett-Teller (BET) surface areas (Table S1). Accordingly, such a change trend of photocatalytic activities was hardly affected by surface morphologies and surface areas, and could be explained as follows. With the increase of  $x$  to 0.3, the gradually narrowed bandgaps of samples determined the extended absorption of visible light from band-to-band transition as evidenced by UV-Vis results and thus enhanced the photoexcitation to generate charge carriers; and moreover, the increased lattice distortion of samples, as proved by XRD, FTIR and Raman results, would induce stronger dipole moments,<sup>32,33</sup> and thus generate stronger local internal fields that could significantly promote the separation and migration of charge carriers.<sup>1,32-35</sup> Consequently, both the narrowed bandgaps and increased lattice distortion of samples resulted in the improved photocatalytic activities. Nevertheless, with the further increase of  $x$  from 0.3, the visible-light absorption from band-to-band transition showed little change as evidenced by UV-Vis results, and the lattice showed little further distortion as proved by XRD results that the (121) diffraction peaks appeared almost at the same position, thus indicating both the bandgaps and lattice distortion rarely contributed to the further change of photocatalytic activities. The gradual decrease of photocatalytic activities with the further increase of  $x$  could be attributed to the increased amounts of  $\text{Cr}^{6+}$  and defects as proved by the XPS and UV-Vis results, respectively, since both  $\text{Cr}^{6+}$  and defects were generally acted as the recombination centers of charge carriers and thus were detrimental to photocatalytic H<sub>2</sub> evolution.<sup>27,28,30,31</sup> In order to further improve the photocatalytic activities of as-prepared  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions, systematic investigations on the reduction of  $\text{Cr}^{6+}$  and defects are in

progress. For example, melamine was mixed with the as-prepared  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions and decomposed to form  $\text{g-C}_3\text{N}_4/(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  composites by a one-pot pyrolysis process, during which the reducing atmosphere and surface covering could effectively diminish  $\text{Cr}^{6+}$  and defects. The results will be reported soon.

In addition, cyclic tests of photocatalytic activities were performed in order to check the photocatalytic stability of samples, and the typical result from NaLaTiCrO-0.30 is shown in Fig. 6b. The photocatalytic activity of NaLaTiCrO-0.30 showed little decrease in 3 cyclic tests for 18 h, thus demonstrating the good photocatalytic stability of the as-prepared  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid-solution photocatalysts for visible-light-driven H<sub>2</sub> evolution.

## Conclusions

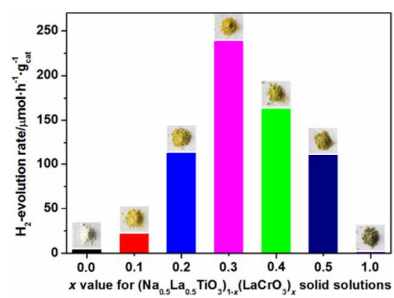
A series of continuous  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions with orthorhombic-phase perovskite structure and with  $\text{LaCrO}_3$  contents ( $x$ ) in the range from 0 to 1.0 were synthesized by a facile PC method instead of the hydrothermal method employed in our previous work, in order to optimize the physicochemical properties by adjusting the chemical compositions over a larger range and thus further improve the photocatalytic for H<sub>2</sub> evolution under visible-light irradiation. It was found that photocatalytic activities of the solid solutions significantly increased with the increase of  $x$ , and reached the highest H<sub>2</sub>-evolution rate of  $238.2 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$  on  $(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{0.7}(\text{LaCrO}_3)_{0.3}$ , and then gradually decreased with the further increase of  $x$ . With the increase of  $x$ , on the one hand, the narrowed bandgaps of samples enhanced the generation of charge carriers and the increased lattice distortion of samples could promote the separation and migration of charge carriers, thus contributing to the improvement of photocatalytic activities; on the other hand, the gradually increased amounts of  $\text{Cr}^{6+}$  and defects accelerated the recombination of charge carriers, thereby resulting in the reduction of photocatalytic activities.

## Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 51302212), the China Postdoctoral Science Foundation (Nos. 2014T70915 and 2013M540745), the Natural Science Basic Research Plan in Shaanxi Province of China (No. 2014JQ2-5022), and the Postdoctoral Science Foundation in Shaanxi Province of China, and the Fundamental Research Funds for the Central Universities (2013jdhz20).

## Notes and references

- J. W. Shi and L. J. Guo, *Prog. Nat. Sci. Mater. Int.*, 2012, **22**, 592-615.
- T. Hisatomi, J. Kubota and K. Domen, *Chem. Soc. Rev.*, 2014, **43**, 7520-7535.
- S. J. A. Moniz, S. A. Shevlin, D. J. Martin, Z. X. Guo and J. W. Tang, *Energy Environ. Sci.*, 2015, **8**, 731-759.
- W. Q. Cui, Y. F. Liu, L. Liu, J. S. Hu and Y. H. Liang, *Appl. Catal. A*, 2012, **417**, 111-118.
- L. Liu, Y. H. Qi, J. S. Hu, Y. H. Liang and W. Q. Cui, *Appl. Surf. Sci.*, 2015, **351**, 1146-1154.
- Z. G. Zou, J. H. Ye, K. Sayama and H. Arakawa, *Nature*, 2001, **414**, 625-627.
- A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37-38.
- K. Maeda, K. Teramura, D. L. Lu, T. Takata, N. Saito, Y. Inoue and K. Domen, *Nature*, 2006, **440**, 295-295.
- X. B. Chen, L. Liu, P. Y. Yu and S. S. Mao, *Science*, 2011, **331**, 746-750.
- J. Liu, Y. Liu, N. Y. Liu, Y. Z. Han, X. Zhang, H. Huang, Y. Lifshitz, S. T. Lee, J. Zhong and Z. H. Kang, *Science*, 2015, **347**, 970-974.
- K. K. Sakimoto, A. B. Wong and P. D. Yang, *Science*, 2016, **351**, 74-77.
- A. Kubacka, M. Fernandez-Garcia and G. Colon, *Chem. Rev.*, 2012, **112**, 1555-1614.
- E. Grabowska, *Appl. Catal. B*, 2016, **186**, 97-126.
- J. W. Shi, J. H. Ye, Z. H. Zhou, M. T. Li and L. J. Guo, *Chem. Eur. J.*, 2011, **17**, 7858-7867.
- US Pat.*, 3330697, 1967.
- M. Kakihana, *J. Sol-Gel Sci. Technol.*, 1996, **6**, 7-55.
- M. Kakihana, M. M. Milanova, M. Arima, T. Okubo, M. Yashima and M. Yoshimura, *J. Am. Ceram. Soc.*, 1996, **79**, 1673-1676.
- I. Tsuji, H. Kato, H. Kobayashi and A. Kudo, *J. Am. Chem. Soc.*, 2004, **126**, 13406-13413.
- K. Maeda and K. Domen, *Chem. Mater.*, 2010, **22**, 612-623.
- S. Tan, S. Yue and Y. H. Zhang, *Phys. Lett. A*, 2003, **319**, 530-538.
- P. Jayabal, V. Sasirekha, J. Mayandi, K. Jeganathan and V. Ramakrishnan, *J. Alloys Compd.*, 2014, **586**, 456-461.
- S. Saïd, *Mater. Lett.*, 2004, **58**, 1405-1409.
- Y. Li, S. Qin and F. Seifert, *J. Solid State Chem.*, 2007, **180**, 824-833.
- M. N. Iliev, A. P. Litvinchuk, V. G. Hadjiev, Y. Q. Wang, J. Cmaidalka, R. L. Meng, Y. Y. Sun, N. Kolev and M. V. Abrashev, *Phys. Rev. B*, 2006, **74**.
- B. Tiwari, A. Dixit, R. Naik, G. Lawes and M. S. R. Rao, *Appl. Phys. Lett.*, 2013, **103**.
- S. J. L. Billinge and I. Levin, *Science*, 2007, **316**, 561-565.
- D. F. Wang, J. H. Ye, T. Kako and T. Kimura, *J. Phys. Chem. B*, 2006, **110**, 15824-15830.
- J. W. Shi, S. H. Shen, Y. B. Chen, L. J. Guo and S. S. Mao, *Opt. Express*, 2012, **20**, A351-A359.
- A. Nashim and K. Parida, *J. Mater. Chem. A*, 2014, **2**, 18405-18412.
- A. Kudo, K. Omori and H. Kato, *J. Am. Chem. Soc.*, 1999, **121**, 11459-11467.
- J. W. Shi, J. H. Ye, Q. Y. Li, Z. H. Zhou, H. Tong, G. C. Xi and L. J. Guo, *Chem. Eur. J.*, 2012, **18**, 3157-3162.
- H. Nishiyama, H. Kobayashi and Y. Inoue, *ChemSusChem*, 2011, **4**, 208-215.
- J. W. Shi, J. H. Ye, L. J. Ma, S. X. Ouyang, D. W. Jing and L. J. Guo, *Chem. Eur. J.*, 2012, **18**, 7543-7551.
- Y. Inoue, *Energy Environ. Sci.*, 2009, **2**, 364-386.
- L. Q. Jiang, Y. H. Zhang, Y. Qiu and Z. G. Yi, *RSC Advances*, 2014, **4**, 3165-3170.



$(\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3)_{1-x}(\text{LaCrO}_3)_x$  solid solutions showed enhanced visible-light-driven photocatalytic activities for H<sub>2</sub> evolution due to the narrowed bandgaps and increased lattice distortion.